



2'-Hydroxy-4'-Methoxychalcone Oxime [HMCO] as A Gravimetric and Spectrophotometric Reagent for The Determination of Cu(II)

KEYWORDS

Analytical reagent, Cu(II) chelate, 2'-Hydroxy-4'-methoxychalcone oxime (HMCO)

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ABSTRACT The ligand 2'-Hydroxy-4'-methoxychalcone oxime (HMCO) was developed as a gravimetric and spectrophotometric reagent for the determination of Cu(II). In the pH range of 3.0 to 6.0 this reagent gives brown complex with Cu(II). Job's method of continuous variation and Yoe and Jones mole ratio method revealed the stoichiometry of the complex to be 1:2 [M:L]. The obeyance of Beer's law was studied and the molar absorptivity and Sandell's sensitivity were calculated. The reagent and its complex have been characterized by elemental analysis and IR spectra. From TGA, the energy of activation was also calculated using Broido method for the first step decomposition. The reagent has been used for the determination of Copper content in Brass alloy.

INTRODUCTION :

In the current scenario, large number of organic reagents have been employed for the detection and quantitative determination of metal ions. They include o-hydroxy ketoximes¹⁻², phenyl hydrazones, thiosemicarbazones, chalcone oximes³⁻¹³ etc. These are generally used for spectrophotometric and gravimetric determination of transition metal ions. Here, we report the use of 2'-Hydroxy-4'-methoxychalcone oxime [HMCO] as an analytical reagent for Cu(II).

EXPERIMENTAL :

Instruments :

Spectrophotometric measurements were done on a "Milton Roy" (Spectronic 20D+) Spectrophotometer and "Abotta make UV-1100, UV-Visible Spectrophotometer". The IR spectra were recorded on "Perkin-Elmer" FTIR Spectrophotometer (RX-1) in KBr pallet. The NMR spectra were recorded on "Bruker Avance II 400 NMR Spectrometer. All pH measurements were done on Equip-Tronic pH meter (Model No.EQ 614).

Stock solution :

Stock solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.05 M) was prepared by dissolving 3.121 gm of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (A.R.) in minimum quantity of water and diluted to 250 ml with doubly distilled water. Concentrated sulphuric acid was added in little amount to prevent the hydrolysis of the salt. It was used after standardization¹⁴ with EDTA.

Synthesis of Reagent [HMCO] :

Resacetophenone was prepared from resorcinol, glacial acetic acid and anhydrous zinc chloride according to the method of R. Robinson and R. C. Shah¹⁵. Resacetophenone was treated with methyl iodide and anhydrous potassium carbonate in acetone on a water bath at 65-70°C for six hours. On acidification with dilute HCl, 2-hydroxy-4-methoxy acetophenone was obtained. The 2-hydroxy-4-methoxy acetophenone was converted to chalcone by its condensation with benzaldehyde in presence of aqueous KOH for 24 hours at room temperature. The 2'-hydroxy-4'-methoxychalcone was converted to its oxime using hydroxylamine hydrochloride and sodium acetate. On crystallization from alcohol pure oxime in the form of light yellow crystals with m.p.85°C was obtained. Stock solution of reagent (0.05 M) was prepared by dissolving in 70% aqueous ethanol.

GRAVIMETRIC DETERMINATION OF CU(II) :

Copper sulphate solution (0.05 M, 10 ml) was taken in a clean beaker and diluted to about 100 ml with distilled water. A little excess of reagent solution was added (0.05 M, 22 ml). The

pH of the solution was adjusted between 3.0 to 6.0 using suitable acid buffer. A brown precipitate obtained were digested on water-bath for 60 minutes at 60°C. The precipitate were filtered through a previously weighed sintered glass crucible (G_4) and washed with warm water followed by 70% aqueous ethanol to remove excess of the reagent. The chelate was dried to constant weight at 110°C in hot air oven, cooled and weighed as $\text{Cu}(\text{C}_{16}\text{H}_{15}\text{O}_3\text{N})$. Duplicate experiments were performed in each case. The results are given in Table 1. The experiment was repeated at different pH of solution. The experiment was also repeated with different aliquots, keeping the optimum pH value to evaluate its applicability. The error in any case did not exceed 1.0%.

INTERFERENCE FROM OTHER IONS :

To study the effect of foreign ions on gravimetric determination of Cu(II), 8-10 mg of various cations were added to a solution containing 31.77 mg Cu(II) at pH 5.0 and gravimetric estimations were done. It was observed that Sr(II), Ca(II), Ni(II), Zn(II), Ba(II), Cd(II), Mn(II) and Mg(II) do not interfere at this pH but Fe(III) and Pd(II) interfered seriously. Interference of Fe(III) can be removed by masking it with H_3PO_4 . Many common anions like nitrate, nitrite, sulphate, chloride, bromide, iodide were not found to interfere.

TABLE - 1
GRAVIMETRIC DETERMINATION OF CU(II) USING HMCO

Cu(II) taken = 31.77 mg

Drying temperature = 110-115°C

Salt = $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

pH	Cu(II) complex in g	Cu(II) found in mg	Error	
			in mg	%
3.0	0.3000	31.65	-0.12	-0.37
3.0	0.2999	31.64	-0.13	-0.40
3.5	0.3002	31.67	-0.10	-0.31
3.5	0.3004	31.69	-0.08	-0.25
4.0	0.3005	31.70	-0.07	-0.18
4.0	0.3007	31.72	-0.05	-0.15
4.5	0.3010	31.75	-0.02	-0.06
4.5	0.3012	31.76	-0.01	-0.03
5.0	0.3014	31.79	+0.02	+0.06
5.0	0.3015	31.80	+0.03	+0.12
5.5	0.3020	31.86	+0.09	+0.28
5.5	0.3018	31.83	+0.06	+0.18
6.0	0.3025	31.91	+0.14	+0.44
6.0	0.3022	31.88	+0.11	+0.34

Conversion factor = 0.1055

SPECTROPHOTOMETRIC STUDY OF CU(II)-HMCO CHELATE :

5 mg of chelate was extracted in 25 ml of chloroform and the absorption spectra was recorded in the range of 300 to 800 nm. It was observed that the absorbance of the coloured solution of chelate increases continuously towards the shorter wavelength. A weak band is observed at 400 nm and hence all measurements were carried out at 400 nm.

VERIFICATION OF BEER'S LAW AND OPTIMUM CONCENTRATION RANGE :

To 5 ml of solution (0.01 M) of the reagent HMCO, varying amount of the Cu(II) solution (0.005 M) was added and the pH was adjusted to 5.0, using $[\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}]$ buffer. The insoluble complex was extracted in chloroform using three 5.0 ml, portions of chloroform and final volume of chloroform extract was adjusted to 25.0 ml. The absorbances of these solutions were measured at 400 nm against chloroform as blank. Absorbance values were plotted against metal concentration expressed in ppm. A straight line passing through the origin, indicating obeyance of Beer's law is obtained up to 38.12 ppm of Cu(II). The molar absorptivity of the Cu(II)-HMCO complex was found to be $6.716 \times 10^2 \text{ lit. mol}^{-1} \cdot \text{cm}^{-1}$ and the Sandell's sensitivity is found to be $0.0946 \mu\text{g}/\text{cm}^2$ at 400 nm.

STOICHIOMETRY OF COMPLEX :

Job's method of continuous variation¹⁶ and Yoe and Jones mole ratio method¹⁷ were used to determine the stoichiometry of the Cu(II)-HMCO complex. From both the methods, it was found to be 1:2 [M:L] ratio. This is in agreement with the stoichiometry found from gravimetry. The average stability constant found from two methods is 4.065×10^8 . The Gibb's free energy change for complex formation reaction at 30°C was found to be -11.81 K.cal/mole.

IR SPECTRA :

Examination of the IR spectra of the chelates show that the band due to intramolecular hydrogen bonded O-H stretching of 2-hydroxy group disappears in the Cu(II)-HMCO complex while the band due to oximino -OH group at 3429 cm^{-1} in Cu(II) chelate.

The band due to the -C=N stretching which is observed at 1548 cm^{-1} in ligand is shifted to $1507\text{-}1608 \text{ cm}^{-1}$ in complexes. This may be due to coordination of metal through nitrogen. This is further supported by slight downward shift of νNO from 1029 cm^{-1} in the ligand to 959 to 982 cm^{-1} in copper chelate. Thus, in the chelate, metal is covalently bonded with oxygen and coordinate bonded with nitrogen.

GRAVIMETRIC ESTIMATION OF CU(II) IN BRASS ALLOY USING HMCO :

Preanalysed sample of brass (0.5523g) was dissolved in 50% HNO_3 by heating for 30 minutes. The solution is evaporated to a volume of near about 5 ml but not to dryness and the bulk of nitric acid removed. The resulting solution was diluted to 100 ml with doubly distilled water in volumetric flask.

An aliquot of above diluted solution (10 ml) was taken in a clean beaker and copper was determined gravimetrically using 2'-hydroxy-4'-methoxychalcone oxime (HMCO) as per the procedure described previously.

RESULTS :**ESTIMATION OF COPPER :**

1. Weight of Cu(II)-HMCO complex = 0.3842 gm
2. Copper found in 10 ml diluted solution (Average of three determinations) = 0.04058 gm
3. Copper found in brass alloy sample = 0.4058 gm
4. Percentage of copper found in brass alloy sample = 73.47%
5. Percentage of copper reported in brass alloy sample = 73.40 %
6. Percentage error = -0.095 %

THERMOGRAVIMETRIC ANALYSIS (TGA) STUDY OF CU(II)-HMCO COMPLEX :

From the result of TGA, it is seen that the complex is stable upto temperature 150°C and so it can be dried safely without decomposition at $100\text{-}150^\circ\text{C}$. The loss in weight in the temperature range 150°C to 800°C is due to the removal of organic ligand molecule. The observed loss agrees well with the loss expected as per formula of the chelate in which M:L ratio is 1:2. The weight of residue agrees with the weight of residue expected as per the given formula. This confirms the metal:ligand ratio [1:2] which is also established from the results of gravimetric analysis, elemental analysis and spectrophotometric methods. Activation energy E_a was calculated using Broido method¹⁸.

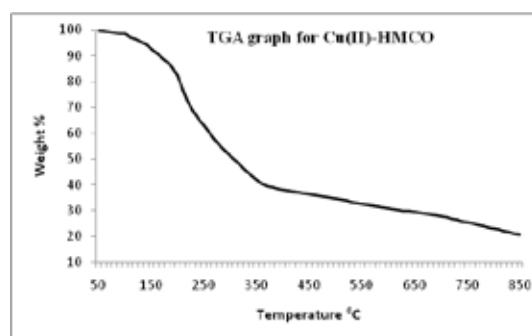


Fig. (I) : TG Curve of Cu(II)-HMCO Complex

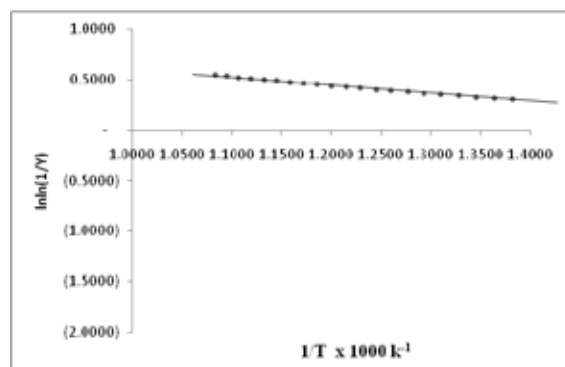


Fig. (II) : Method of Broido : Cu(II)-HMCO Complex

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REFERENCE

1. A.B.Bhatt and K.K.Desai, J.Inst.Chemists (India), (1989), 61, 5.
2. D. Vijaykumar, R.C.Hussain and N. Appala Raju, J. Indian Chem. Soc., 67, (1990), 786.
3. S. K. Shingadia and K. K. Desai, (2007), E-Journal of Chemistry, 4(1), 97- 102.
4. Miss Krishna Purohit and K. K. Desai (2005), E-Journal of Chemistry, 2(2), 161-164.
5. J.J.Desai, P.G.Desai and A.G.Mehta (1999), Asian J. Chem., 11(2), 519.
6. Sayaji Rao M., Prasad N. B. L. and Hussain Reddy K. (2006), Indian Journal of Chemistry, Sec.-A: Inorganic, Physical, Theoretical & Analytical, 45(7), 1659-1662.
7. Ambily P. Nair and J. Christine, E-Journal of Chemistry, 2009, 6(2), 303-307.
8. Ambily P. Nair and Christine Jeyaseelan, Pelagia Research Library, Der Chemica Sinica, 2010, 1(3), 100-106.
9. Ambily P. Nair, Christine J. and K. K. Desai (2008), Oriental Journal of Chemistry, 24(2), 693-696.
10. Satheesh K. P., Ravichandran. S, Rao V. Suryanarayana, Devanna N., Chandrasekhar K. B., (2011), International Journal of ChemTech Research, 3(4), 1740-1746.
11. Nitinkumar B. Patel, Nirav Hiteshkumar Parekh (2012), Oriental Journal of Chemistry, 28(4), 1815-1819.
12. Nilesh G. Limbachiya and K. K. Desai (2013), International Journal of ChemTech Research, 5(5), 2347-2350.
13. Nilesh G. Limbachiya and K. K. Desai (2013), Journal of Chemical, Biological and Physical Science, 3(4), 2435-2437.
14. Nilesh G. Limbachiya and K. K. Desai (2013), Journal of Chemical, Biological and Physical Science, 3(4), 2498-2504.
15. Nilesh G. Limbachiya and K. K. Desai (2014), International Journal of ChemTech Research, 6(1), 786-789.
16. Vogel A. I., "A Text-Book of Quantitative Inorganic Analysis", Longmans Green and Co., 1961.
17. R. Robinson and R. C. Shah (1934), J. Chem. Soc., 1934.
18. Job P., Ann. Chem., 1928, 9, 113.
19. Yoe and Jones A. L., Ind. Eng. Chem. and Edn., 1944, 16, 111.
20. Broido A. (1969), J. Polym. Sci., Part A-2, 7, 1761.